The Liquid State

2. Its Structure and Dynamics

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The liquid state is more complicated than either the gaseous or the solid crystalline state. However, using X-ray and neutron diffraction on the one hand and computer simulation on the other, detailed information has been obtained on the structure and dynamics of the liquid state.

Modelling of Liquids

There are various models proposed in the literature for a liquid. These are (a) hard sphere model, (b) the lattice gas model, (c) the defect solid state model and (d) Bernal's model of random close packed structure.

In the hard sphere model, the particles of the liquid are taken to be hard spheres but with a long range attractive force. Such a model mimics many of the properties of the liquid including the existence of a triple point at which the solid, liquid and gas phases coexist. This is a favourite model for computer experiments.

In the lattice gas model, one assumes a network of periodic cells in a lattice as in a crystalline solid. However not all cells are occupied by a particle of the liquid. This model is mathematically attractive and can be handled in the same way as the *Ising model* for a ferromagnet.

The lattice gas model is an example of a defect solid state model in which one introduces vacancies at random in a lattice. One may introduce more complicated defects like random dislocation networks in the lattice to simulate a liquid.

The random close packing model was obtained by a real life

experiment. Bernal and co-workers filled a balloon with thousands of steel ball bearings. After squeezing and shaking the balloon until they were satisfied that random close packing was achieved, they poured some paint inside. The balls had light coating of grease; hence the paint ran off the balls except in places where the balls actually touched or had a very small gap (about 5% of the diameter of the ball). When the paint was dry the balls were removed from the balloon and a statistical count of the number of paint rings and dots were obtained. From this the coordination numbers and the radial distribution functions were obtained. One important conclusion was that in random close packing the coordination number was around eight with a statistical distribution. In the ideal close packed structure in a crystal this number is twelve.

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Later Scott at Toronto created a computer replica of a heap. A detailed analysis of this replica showed that the radial distribution function for random close packing is essentially the radial distribution function for a liquid.

In the eighteenth and nineteenth centuries, mathematicians carried out the study of coordination numbers in terms of geometry of neighbours. This was done using the concept of *Voronoi polyhedra*. Take a point and bisect the line joining it to its neighbours with planes. The smallest polyhedron enclosed by the planes is called the Voronoi polyhedron for the given point. A set of all Voronoi polyhedra fill up space. One can make foam rubber models of these 'canonical' polyhedra and fill up space with them to make a model of a liquid.

Multicomponent Liquids

We have considered so far a single component liquid. But one often meets with liquid mixtures containing two, three or more components. In the simplest case of a binary (two component) mixture AB, one has to deal with three partial pair correlation functions $g_{AA}(r)$, $g_{AB}(r)$ and $g_{BB}(r)$. $g_{AB}(r)$ gives the neighbours of type B to an atom of type A. It will not be possible to derive the

three pair correlation functions using a single diffraction picture obtained with say X-rays. One should compliment this data by use of other radiations for obtaining diffraction pictures. Neutrons are suitable for this purpose as they have a large penetrative power. Also the scattering power of different atoms for neutrons is very different from the scattering power of the same atoms for X-rays. The scattering power of two isotopes of the same element can be very different for neutrons whereas for X-rays it is the same. One can therefore get two diffraction patterns with neutrons (on samples with and without substitution of isotopes) and one X-ray diffraction pattern. With three different diffraction patterns one can solve for the three pair correlation functions of a binary liquid. *Figure 1* shows the partial structure factors obtained in this fashion in the case of liquid Cu_6–Sn_5 alloy.

It is obvious that the complexity increases when the number of components in the alloy is more than two.

Dynamics of Liquids

In a liquid the atoms are moving continuously. The structure of liquids that we have been discussing is a time-averaged structure. But it will be interesting to study the complicated molecular motions experimentally.

Glauber and Van Hove independently generalised the pair correlation function to take time dependence into account. This generalised function $G(\mathbf{r}, t)$ has the following significance. Given an atom at the origin at time 0, $G(\mathbf{r}, t)$ gives the probability of finding an atom at $\mathbf{r}$ at time t. Since we are dealing with different instants of time, a contribution to $G(\mathbf{r}, t)$ may come from a different atom at position $\mathbf{r}$ at time t or from the same atom moving from the origin to position $\mathbf{r}$ at time t. Corresponding to this generalised pair correlation function, we have a generalised scattering factor $S(Q, \omega)$ defined by

$$S(Q, \omega) = \iint d\mathbf{r}\, dt \exp[i(Q.\mathbf{r} - \omega t)]G(\mathbf{r}, t) .$$

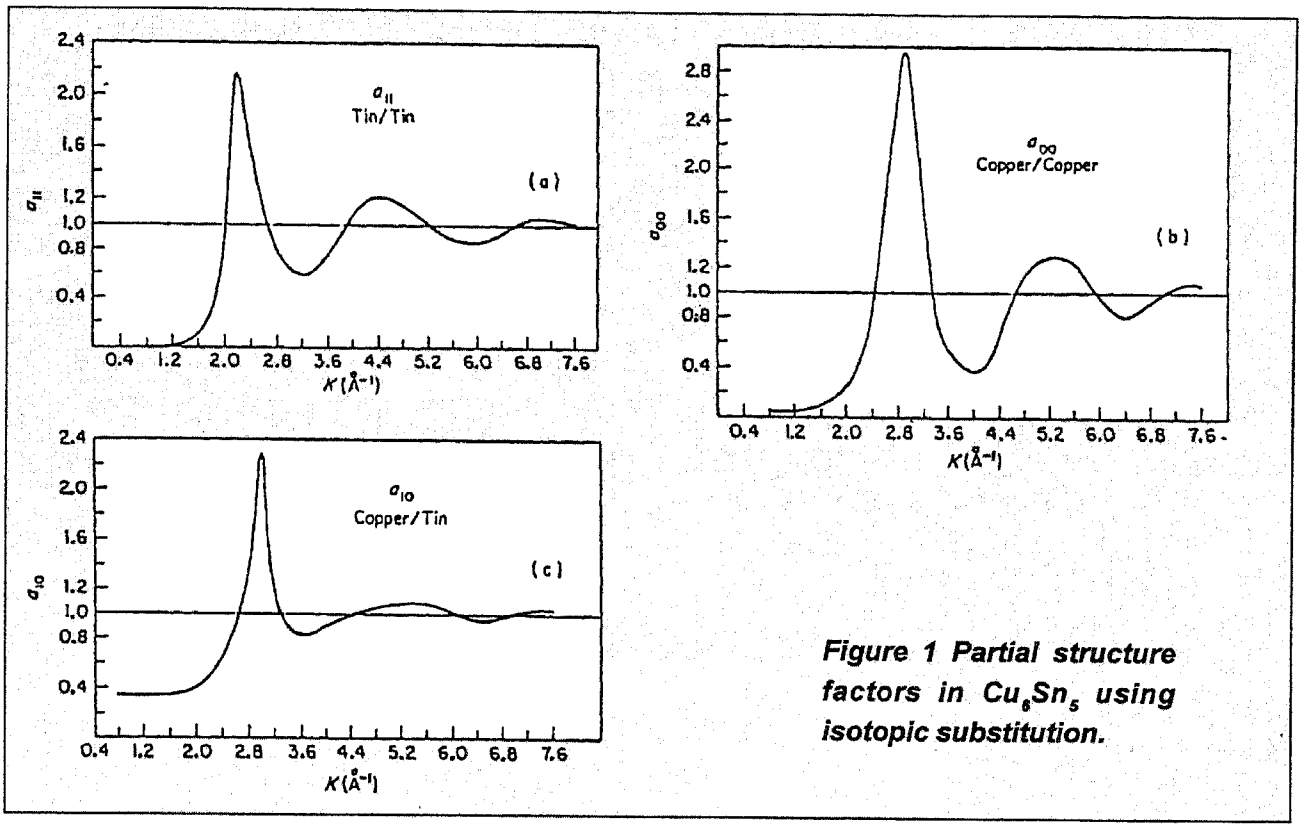

Figure 1 Partial structure factors in Cu_6Sn_5 using isotopic substitution.

Just as Q represents the change in the direction of the probe beam after scattering, $\hbar\omega$ represents the change in energy of the probe particle after scattering. ω represents the angular frequency of the fluctuations associated with the dynamics of the atoms and molecules in the liquid.

Since the energy of the probe particle is changed in the scattering process, this is called *inelastic scattering*. The energies associated with the fluctuations are small. If one uses neutrons then the change in energy will be comparable to the original energy of the neutron. So one can measure the change in energy with good accuracy. This is not possible with X-rays. Inelastic neutron scattering is well suited for the study of dynamics of liquids. *Figure 2* shows the dynamic structure factor $S(Q, \omega)$ measured in liquid argon. From this, using Fourier inversion techniques, one gets the self- and different-atom correlation functions, G_s and G_d as a function of r at different times. This is shown for small, intermediate and large times in *Figure 3*. One sees that G_s

Figure 2 Dynamic structure factor in liquid argon.